2.1 Materials

Distilled water having a conductivity less than 1 $\mu$mho/cm at 303 K was used throughout the study. The hardwood portion of jackwood timber was used as precursor material for the preparation of active carbons, formaldehyde polymerized wood and polyacrylamide grafted wood. The hardwood portion of jackwood was collected from a wood processing industry.

2.1.1 Adsorbents

Activated carbons prepared from wood and modified wood were used as adsorbents. These are well characterized sorbents differing in their surface properties and functionality. The individual particle size of the adsorbent used for the study ranges from +40 to −80 mesh for carbons and +80 to −120 mesh for polymerised wood samples.

2.1.2 Chemicals

All the chemicals used were of analytical reagent grade, with almost 99.9% purity specified by the manufacturer and were obtained from Fluka, BDH and E. Merck. The standard solutions of phenol (P) and $p$-nitrophenol (PNP) were prepared by dissolving the organic solutes in distilled water. Standard solutions of metals, $\text{Pb}^{2+}$, $\text{Hg}^{2+}$ and $\text{Cd}^{2+}$ were prepared from their nitrate salts [E. Merck India Ltd.]. Standard solutions of $\text{Cr}^{3+}$ and $\text{Cr}^{6+}$ were prepared by dissolving $\text{CrCl}_3\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ respectively in water containing $2\text{N}$ acid.
2.1.3 Glasswares

All the glasswares were cleaned with concentrated chromic acid or potassium hydroxide solution followed by rinsing with distilled water.

2.1.4 Instruments

*Infrared Spectroscopy:* FTIR studies were conducted on a Bruker IFS 66 V spectrophotometer at room temperature.

*Diffraction:* X-Ray diffraction studies of carbons were done on diffraction analyser (Rad IIA) manufactured by Rigaku Co. Ltd. (Japan) and wood on a Philips W 1710 diffractometer.

*Scanning Electron Microscopy:* SEM morphological observations were done on a LEICA (Cambridge, U. K) Stereoscan - 260, Scanning Electron Microscope.

*N₂ Gas Adsorption:* The adsorption isotherms for N₂ were determined using a low temperature, volumetric nitrogen adsorption apparatus (Quantasorb, manufactured by Quantachrome, New York) at 77 K.

*CO₂ Gas Adsorption:* The adsorption isotherms for CO₂ were determined at 298 K using a laboratory volumetric apparatus.

*Thermogravimetric Analysis:* Thermaogravimetric curves (TGA/DTG) of the adsorbents were recorded on a Schimadzu TGA – 50H Thermal Analyser at a heating rate of 10°C/min under nitrogen atmosphere.

*Elemental Analysis:* The elemental (CHN) analysis were carried out on a Erlo-Carba model CHN analyser.

*Spectrophotometry:* A Bausch and Lomb spectronic 21D(uv-visible) spectrophotometer was used for the estimation of phenol, p-nitrophenol and metals such as Hg²⁺, Pb²⁺, Cd²⁺, Cr³⁺ and Cr⁶⁺.

*Bath Incubator:* A shaking water bath-incubator (Remi-model - G - 16) having a temperature variation of ±1.0° was used for all the equilibrium studies.

*pH meter:* An Elico (India) model L1-120 pH meter was used to measure pH.
2.2 Methods

2.2.1 Preparation of Carbons

2.2.1.1 Activation of Wood with ZnCl₂

The *Katha* wood (hardwood or porouswood) in the form of dust was collected from a wood processing industry. It is dried at 373±5 K in a hot air oven for 24 hrs. The laboratory scale activation was done by the procedure as described earlier [32]. ZnCl₂ was incorporated to increase the yield and porosity of the resulting carbon. The precursor after a contact time of 6 hrs with activating Zn²⁺ solution was carbonised in the inert atmosphere of a temperature programmed furnace.

A batch of 300.0 g of oven dried dust is digested in 500 ml of hot boiling concentrated ZnCl₂ solution (analar grade Merck, India) in a flask. The amount of ZnCl₂ used for impregnation depends on the ratios (1) $X_{Zn^{2+}}$ or simply $X_{Zn}$ (grams of Zn per gram of wood) or (2) $I_{ZnCl_2}$ (grams of ZnCl₂ per gram of wood). $X_{Zn^{2+}}$ is defined as the weight of Zn²⁺ (as ZnCl₂) used for loading divided by the weight of basic carbonaceous precursor. The digested material is consolidated layer by layer and filled up to the brim of a steel container with tightly fitting lid for ensuring minimum entrapped air in the voids. Arrangements were done for achieving total absence of air to control the carbonization in inert atmosphere [137]. The container was placed in an electrical muffle furnace and was heated at a rate of 5 K/min.

On attaining the chosen desired activation temperature, the system was maintained for 6 hrs as such to ensure the complete carbonization. The amount of Zn²⁺ incorporated has a direct influence on the development of porosity. Polymeric cellulose or lignin, during pyrolysis, liberates most of the non-carbon elements mainly hydrogen, oxygen and nitrogen in the form of gases and tars.

To find the extent of carbonization and optimum temperature in terms of carbon yield, three different batches of samples were carbonised at a temperature ranging from 373 K to 1173 K. The carbonization was done in nine sets or batches. When carbonization is completed the content (carbonised char) is digested in hot solution of 1.5 N HCl (500 ml) in a round bottomed flask thrice. The content separated and washed using water under vacuum till the washings are free from Zn²⁺ ions and constant pH 7.0 is attained. Regeneration of Zn²⁺ loaded during activation is completed. In all conditions, the yield of charbon (char) was calculated and reported as unit weight of activated carbon (C+Zn-Zn) to the weight of wood (WD) dry weight.

2.2.1.2 Preparation of carbon CS

Sulphuric acid activated carbon (CS) was prepared by a procedure as described earlier [138]. About 300 g of wood (+40 to –60 mesh) was treated with 1.8 parts by weight of concentrated sulphuric acid (A. R. Merck, 98%, density, 2.8) in an acid resistant ceramic container. It was heated in an electrical furnace at 523±5 K for
24 hrs in the absence of air. Char was washed with hot distilled water to remove the free acid under vacuum, till the washings are free from sulphate ions. This carbon is referred as CS.

2.2.1.3 Washing and Drying of Carbons

ZnCl$_2$ activated carbons, after regeneration of loaded Zn$^{2+}$ in hot 1.5 N HCl and continuous washing with distilled water was subjected to a further washing according to a standard procedure [94]. The carbon was packed into a glass column (diameter 3 cm, length 130 cm). It was washed with 10 bed volumes of 0.5 M aqueous NaOH solution using a peristatic pump. Sufficient bed volumes of distilled water was passed to remove the traces of alkali left till pH 7.0 is noted in the washings. Then the washing is repeated with 10 bed volumes of 0.5 M HCl. Finally, the required bed volumes of distilled water is passed until a neutral pH was noted.

The washing process was repeated for sulphuric acid activated (CS) and carbon obtained by heating wood in the absence of air and an activating agent at 725 K, referred as pseudoactivated (CA) carbon. The washings of CS with NaOH is coloured (dark brownish) due to the dissolution of mesophase tar. This is a mixture of all the condensable, semi-volatile and nonvolatile compounds formed during the incomplete pyrolysis of bio-mass [85]. The washed carbons were collected and dried in vacuum at 373 K, so that physisorbed water was ensured to be negligible.

2.2.1.4 Modification of carbon CZ1

The oxidation of carbons was done by the modified method of Vinke[94]. Fifteen grams of dry carbon were added to a three necked round bottomed flask of capacity 250 ml. It is equipped with a stirrer, a condenser, and a dropping funnel and contains a calculated quantity of water so that the total volume of the reaction medium is 100 ml. After the mixture was heated to reflux, a calculated amount of HNO$_3$ (69%, density = 1.45) was added through the funnel. The reaction was completed within 2–5 hrs. The yield was noted after oxidation on dry weight basis.

Oxidation with 25.88% HNO$_3$: The reaction mixture consists of 62.5 ml distilled water, 15.0 g of carbon (CZ1) and 37.5 ml of concentrated nitric acid. Reflux was continued for 2 hrs, thereafter the overlying solution was removed through filtration. The oxidation procedure was repeated by adding another fresh 100 ml of HNO$_3$ and refluxed for 1 hr. The resulting carbon was oxidised two times continuously for the entire three hours duration without any intermediate washings. Content were repeatedly washed with distilled water till pH 7.0 was attained for the washings and was dried at 313 K. The modified carbon is referred as CZ1-26, the last number being the concentration of oxidising agent in percent.
Oxidation with 12.94% HNO3: The oxidation was done in a reaction mixture containing 81.25 ml of distilled water, 15.0 g of CZ1 carbon and 18.75 ml of HNO3 acid. It is refluxed for 3 hrs. After filtration, the procedure was repeated by adding another 100 ml of fresh solution of HNO3 without any intermediate washing for 1 hr. A reaction time of 4 hrs was maintained. The carbon was washed and dried as above. The modified carbon has been described as CZ1-13.

Oxidation with 4.31% HNO3: The oxidation of CZ1 (15.0 g) was carried out with 93.73 ml distilled water to which 6.27 ml conc. HNO3 is already added. The reflux was continued for 3 hrs. After filtration the reaction was repeated with 100 ml of 4.31% HNO3 acid without intermediate washing for 1 hr. The experiment was repeated with the same quantity of HNO3 for another 1 hr. The total reaction time was 5 hrs. Carbon was collected, washed and dried. The product is represented as CZ1-4.

2.2.2 Modification of Carbons CA, CS and CZ2

Attempts were made to oxidise the carbons CA, CS and CZ2 (carbon activated at 723 K with \(X_{Zn^{2+}}\ 0.86\)). On oxidation CA and CS were largely destroyed in the solution. This is probably due to the relatively large amounts of aliphatic carbon structures present in the parent carbon networks. Therefore, no further attempt regarding the oxidation was followed. The carbon CZ2 is structurally similar to CZ1 except in the method of preparation where a higher Zn\(^{2+}\) ion ratio was used. It is oxidised in three batches following the same reaction procedure described for CZ1. The oxidised carbons were designated as CZ2-26, CZ2-13 and CZ2-4.

2.2.3 FTIR Studies

The transmission spectra of samples were recorded using the KBr pellet method. The KBr discs were prepared by the method followed for carbon materials [94]. Here 10 mg of perfectly pre-dried, powdered carbons and wood samples was homogenised with 500 mg of KBr (spectroscopic analar grade, Merck) in an agate mortar. The mixture is dried at 393 K for 1 hr and further diluted by adding 12.5 mg of this mixture with 187.5 mg of KBr. The samples were dried overnight at 373 K in vacuum and pressed. The original spectra were corrected with a curved base-line used for strongly scattering samples, like carbon.

2.2.4 Acid Strength and Acid Sites

The reagents used for the potentiometric method of determining the acid strength and acid sites were pure n-butylamine and acetonitrile (analar, Sigma). The pH was recorded using an Elico digital pH meter with glass and calomel electrodes.
A small quantity of 0.1 N n-butylamine in acetonitrile was added to a suspension of 50 mg of pre-dried, powdered adsorbent (carbon or wood) in 50 ml of acetonitrile and agitated for 6 hrs in a temperature-controlled shaking machine at 293 K. When the content was uniformly dispersed and equilibrium is reached, it was titrated against the same standard solution of n-butylamine in acetonitrile from a microburette at 0.05 ml intervals. The electrode potential variation was noted for each addition. The mass of the solid and the quantity of base used to reach equilibrium depends on the acidity of the solid used. The potential in millivolts is plotted against the amount of butylamine consumed (meq/g).

2.2.5 TGA/DTG Analysis

The thermal characterization of carbon and wood was done by TGA/DTG. The decomposition of carbon and wood was investigated using a Shimadzu TGA - 50 H thermal analyser. About 10 mg of the solid was heated in a fused silica tube oven under a flow of nitrogen at the rate of 10 ml/min and at a heating rate of 10 K/min upto 1473 K. The thermal data is used to elucidate the sources of weight loss. Only quantitative information could be drawn from the plotted TGA and DTG curves.

2.2.6 Boehm Titration

Quantitative base/acid neutralization experiments were conducted for the functionalisation of carbon and wood surfaces. Eleven adsorbent samples were used in the determination of surface functional groups. Acidity constants of carboxyl groups, lactones and phenols present on surfaces of carbon differ over several orders of magnitude [139]. These groups can be distinguished by their neutralization behavior with NaHCO₃, Na₂CO₃, NaOH and n-C₄H₉NH₂. The surface basicity of all the samples was also determined on the basis of HCl consumption. The amount of hydroxylamine hydrochloride consumed is a measure of carbonyl groups and was also evaluated [140, 141, 142].

The samples were titrated with bases of different strengths (NaHCO₃, Na₂CO₃ and NaOH) following Boehm’s method [140]. It is well established [98] that NaHCO₃ titrates only carboxylic groups, Na₂CO₃ titrates carboxyl and lactones and NaOH titrates carboxyl, lactones and phenolic groups. Hence one can obtain the number of different acid groups. Any base present on the surface can be titrated with HCl as described by earlier workers [143].

2.2.6.1 Carboxyls

Most widely accepted and convenient way of determining the concentration of free carboxyl group is to perform neutralization reaction with NaHCO₃. A small quantity (0.150 g) of powdered adsorbent was shaken with 30 ml of 0.05 N NaHCO₃ for 20 hrs. The contents were separated and the filtrate collected. An aliquot of the
solution was mixed with excess of 0.05 N HCl and the CO₂ gas formed was boiled off and back titrated with standard NaOH.

2.2.6.2 Lactones

Lactones are opened by Na₂CO₃. Therefore, 0.05 N Na₂CO₃ solution is suitable for the determination of carboxyl groups in lactone type binding [45]. An amount equal to 150 mg sample was shaken thoroughly with 30 ml of 0.05 M Na₂CO₃ solution for 20 hrs and the contents separated. Aliquot of the solution (10 ml) was mixed with excess of 0.05 M HCl and the CO₂ boiled off and back titrated with standard NaOH solution.

2.2.6.3 Phenols

It is generally assumed that phenolic hydroxyl groups on the carbon surface react with strong alkali (NaOH) analogously to free phenols. In order to estimate the NaOH uptake value 0.150 g of carbon or wood was shaken thoroughly with 30 ml of 0.05 N NaOH for 20 hrs. An aliquot of the filtrate is titrated against standard HCl.

2.2.6.4 Bases

Hydrochloric acid is adsorbed on the basal planes of carbons due to the basic character of aromatic π electrons. The amount of HCl adsorbed equivalent to γ pyrones) [144] was calculated by the same analytical procedure described earlier. About 0.150 g of adsorbent was shaken with 30 ml of 0.05 M HCl and the overlying solution was titrated with standard NaOH.

2.2.6.5 Butylamine Adsorption

N-butyamine adsorption was conducted by the method followed by Puri et al. [145]. An amount equal to 0.500 g of adsorbent was shaken with 50 ml of 0.7 N aqueous solution of analar n-C₄H₉NH₂ in a stoppered bottle for 48 hrs. An aliquot of the supernatant solution was titrated against a standard solution of HCl using bromophenol blue indicator.

2.2.7 Hydroxylamine Adsorption

Hydroxylamine hydrochloride consumption of the solids is estimated by shaking 0.150 g of the adsorbent with 30 ml of NH₂OH.HCl in methanol for 72 hrs at 323 K. A known quantity (10 ml) of the clear filtrate was titrated against alcoholic NaOH using bromophenolblue indicator.

The samples recovered from NaHCO₃, NaCO₃, NaOH, HCl, n-C₄H₉NH₂ and NH₂OH were washed with distilled water and alcohol and dried under vacuum at
373 K for 6 hrs. These samples were further analysed for elemental composition, and infrared spectroscopic studies to describe variations in properties.

2.2.8 Determination of pH\text{ZPC}

Acid/base potentiometric titration was also carried out to obtain the point of zero charge. The titrations were made in 0.001, 0.01, and 0.1 M NaNO\textsubscript{3} solutions. The amount of adsorbents used in each titration was 200 mg. Titration were performed by adding standard solutions of HNO\textsubscript{3} (0.1 M) and NaOH (0.1 M) using calibrated micropipettes. The different amounts of acid or base were added to each bottle. The bottles were then placed on a shaker and allowed to obtain equilibrium for over two days. They were filtered after shaking was finished. These procedures were repeated for different ionic strengths of the NaNO\textsubscript{3} solution 0.1 and 0.001 M. After the equilibration period, the pH recorded after a stable value was obtained using an Elico pH/mv meter. Blank samples, containing NaNO\textsubscript{3} was also titrated. The net Surface Charge Density, $\sigma_0$ was calculated using equation.

$$\sigma_0 = F (C_A - C_B + [OH^-] - [H^+]) / A \tag{1}$$

where $\sigma_0$ is the surface charge density (C/cm\textsuperscript{2}), $A$ is the surface area of the suspension (cm\textsuperscript{2}/l), $C_A$ and $C_B$ are the concentrations of strong acid and alkali after each addition during the titration, $[H^+]$ and $[OH^-]$ are equivalents of H\textsuperscript{+} and OH\textsuperscript{-} bound to the suspension surface (eq/cm\textsuperscript{2}).

2.2.9 Physisorption of N\textsubscript{2} and CO\textsubscript{2}

The adsorption isotherms for nitrogen were determined using a low tempreature volumetric N\textsubscript{2} adsorption apparatus at 77 K. The nitrogen saturation pressure was continually monitored and P/P\textsubscript{o} was recorded accordingly. A liquid density of 0.808 g cm\textsuperscript{-3} has been assigned for nitrogen in the adsorbed phase at 77 K to calculate micropore volumes. In the present calculation, the value of $\beta$ (obtained from molar volume data) is taken as 0.35. Surface area values were estimated from N\textsubscript{2} adsorption isotherms using the BET single and multiple point equations. The adsorption isotherms for CO\textsubscript{2} were determined at 298 K using a laboratory volumetric apparatus [146].

The molecular cross-sectional area of N\textsubscript{2} at 77 K and CO\textsubscript{2} at 298 K were taken as 0.162 and 0.253 nm\textsuperscript{2}, respectively [147]. Prior to the measurement, the adsorbent was outgassed at 383 K for 12 hrs under N\textsubscript{2} flow. Also in CO\textsubscript{2} adsorption experiments, all the samples were first oven dried at 383 K for 12 hrs at a low pressure of about 13 Pa. For each experimental point on the CO\textsubscript{2} adsorption isotherm an equilibrium of one hour was allowed. Surface area from CO\textsubscript{2} adsorption isotherm was estimated using the Dubinin-Radushkevich equation [148].
2.2.10 BET Surface Area

Brunauer et al. (1938) [112] accepted the adsorption of nitrogen at a temperature, close to its boiling point as a standard approach to measure total surface area of solids. A typical apparatus for $N_2$ adsorption isotherm studies made of glass is shown in Figure 2.1.

![Fig. 2.1. BET gas adsorption apparatus.](image)

Procedure: The sample taken in the adsorption cell was attached to the adsorption train. High vacuum grease was applied on the ground-glass connection. Air, water and other interfering impurities were removed by placing a sleeve furnace around the adsorption cell and degassing it under high vacuum for 1 hr at 573 K. The sample was allowed to cool. A Dewar flask filled with the liquid nitrogen was placed around the adsorption bulb. It was connected to a vapour pressure manometer bulb. Using He, the free space in the cell and the space between sample particles were first determined. The gas was admitted to the burette system through stopcock 3.
and the pressure was measured. Then helium was admitted to the adsorption cell through stopcock 6 and the pressure was again measured. From STP relation the initial volume of helium and the volume remaining in the burette system after exposure to the adsorption cell were calculated. The volume of gas which expanded into the free space, \( V_{He} \) was the difference between these two volumes, which vary with pressure. \( V_{He} \) was divided by the corresponding pressure to obtain a constant or adsorption bulb free space factor, \( f_A \). Multiplication of \( f_A \) by the pressure at any time gives the volume of gas, corrected to standard conditions, contained in the adsorption bulb.

**Evaluation of \( V_a \):** The liquid nitrogen bath was removed and helium evacuated from the system. When the McLeod guage indicated a good vacuum, the stopcocks were closed and the liquid nitrogen bath replaced. By lowering the mercury level in the large burette, nitrogen was admitted to the adsorption train. The volume admitted \( V_1 \) was determined from the STP equation. The stop cock 6 to the adsorption bulb was opened. When equilibrium was established the volume of nitrogen \( V_2 \) remaining in the burette system after adsorption was calculated at STP. The volume of nitrogen adsorbed \( V_a \) was determined using the following formula,

\[
V_a = V_1 - (V_2 + V_3)
\]

\[
V_3 = P \times \text{ free space factor}, \quad f_A \times \text{ correction for deviation from ideal gas law}
\]

The recorded vapour pressure of the nitrogen provides the data for the first point in the plot of \( \frac{P}{P_0} / V_a(1 - P/P_0) \) versus \( P/P_0 \) [112]. Additional points were obtained by moving the Hg in the burette upward, thereby increasing pressure. The slope and intercept of the line were determined. The surface area was hence calculated.

### 2.2.11 Grafting of Wood

The hardwood dust procured from a local industry was first refluxed in a r.b. flask. The suspension was filtered, and then subjected to soxhlet extraction with acetone for about 12 hrs. The product was washed with cold distilled water, dried in vacuum at 373 K and stored over activated molecular sieves. Hereafter, the material is defined as native wood. The empirical composition of the material was found to be \( \text{C}_4\text{H}_6\text{O}_3 \).

#### 2.2.11.1 Pre-treatment

Prior to grafting, the wood was extracted in a 1:2 mixture of alcohol and benzene for 8 hrs to dewax the biopolymer. Then it was kept in 17.5% NaOH solution for 30 minite to remove the soluble polyphenols. Again, soxhleted with distilled water,
washed and dried under vacuum. The treated wood was grafted with polyacrylamide using a modified procedure described elsewhere [149, 17].

2.2.11.2 Rate of Grafting

The optimum conditions for grafting of treated wood were studied in detail as a function of monomer concentration, crosslinking agent, temperature, initiator concentration and grafting rate. A mechanism was also suggested for the new natural biopolymeric - polyacrylamide grafted co-polymer. In each case the rate of grafting \( (R_G) \) was calculated using the relationship \( R_G = 100 \times \frac{W_1}{V} \times t \times M \), where \( V \) is the volume of the mixture, \( t \) is the time in seconds, \( M \) is the molecular weight of the monomer and \( W_1 \), is the weight of the original wood.

2.2.11.3 Grafting Procedure

A known amount of wood was added to 50 ml of an aqueous solution of N, N'-methylenebisacrylamide and potassium peroxydisulphate initiator in a flask. To the mixture in solution, the required amount of acrylamide was added and the contents were stirred vigorously at 343 K; The reaction flask was stoppered air tight and kept as such for 1 hr. Contents were washed with distilled water and dried at 353 K. The grafting percent was calculated using the relationship \( (W_2-W_1) \times 100/W_1 \) where \( W_2 \) and \( W_1 \) are the dry weights of grafted wood and the original wood.

2.2.12 Preparation of GWD

Based on the optimum conditions investigated for the graft copolymerization of wood using acrylamide monomer, GWD (Grafted Wood Dust) required for the adsorption experiments were prepared in bulk using a more specific procedure.

About 100.0 g of treated wood was added to an aqueous solution containing N, N'-methylenebismethacrylamide (20 g/l) and potassium peroxydisulphate (10.0 g/l) in a flask. To the mixture, 40.0 g of acrylamide was added and the contents were stirred at 343 K for 1 hr. The grafted product was washed and dried at ambient temperature. The grafting percentage was found to be 68.1%. The rate of grafting \( R_G \) has a value of \( 4.3 \times 10^{-4} \). The polyacrylamine grafted wood is converted into a cationic exchanger through standard procedure.

Prior to conversion to a cationic exchanger, the polymer was refluxed with ethylenediamine continuously for 8 hrs. The product was washed with toluene and dried at 353 K. Equal amount (1:1 wt/wt) of graft co-polymer and succinic anhydride (A. R. Merck 99.0, C₄H₄O₃, MW, 100.08) refluxed at pH 4.0 in a flask for 6 hrs. The excess succinic anhydride was washed out with 1,4-dioxane followed by ethanol. The new material was dried under vacuum and stored in a desiccator over molecular sieves at room temperature. The final product was identified by FTIR spectrum. The product is hereafter referred to as GWD.
2.2.13 Preparation of FWD

One hundred grams of wood was mixed with a solution (2 litres) containing 560.0 ml of formaldehyde (35%) and 0.2 mol/l sulfuric acid. The mixture was stirred for 2 hrs at 323 K. The polymerized wood was filtered and washed thoroughly with de-ionised water till pH 7.0 was attained. It was then dried at 338 K for 3 days continuously and desiccated. It was used as such for characterizations and adsorption studies. The product is designated as FWD.

2.2.14 Phenol Adsorption

The ability of the new carbonaceous adsorbents to remove pollutants was tested using traditional bench scale batch experiments. A laboratory prepared problem water (a solution of phenol or metal) was used to determine the ability of carbon and wood to remove toxins from wastewater.

Selection of Adsorbent: Activated carbons and wood FWD are used as sorbent materials in this research work. The average particle size 284.5 μm for carbon and 150.3 μm for wood which were available in maximum amount, were used. The preparations have already been discussed in previous sections. The characteristics and major chemical or elemental constituents of the carbons used for study are summarized in chapters 3 and 4.

The sieved carbon was washed with distilled water to remove any carbon fines present and dried at 383 K for 24 hrs. The dried carbon was then stored in a sealed bottle along with silica gel to prevent re-adsorption of moisture. The same procedure was followed for the wood, prior to its use in batch experiments.

Selection of Adsorbate: Phenol (P) and p-nitrophenol (PNP) were selected as the organic pollutants in the present study. The selection of these solutes were based on the following criteria.

- Phenols and its substituted derivatives are included in the priority pollutants list.
- These materials are commonly found in industrial wastewaters and ground waters. Moreover, they are aromatic hydrocarbon residues.

Reagents: A stock solution of each adsorbate was prepared by weighing a given quantity of the chemical and dissolving it in an appropriate volume of de-ionised distilled water. Solutions of various concentrations were prepared by dilution of stock solution. Phenol and p-nitrophenol used in the present study were of analytical reagent grade (99.99% pure) sample supplied by E. Merck. In addition to buffer background solution, a concentration of HgCl₂ (10⁻⁵ M) was used to minimise biological activity during equilibration.
2.2.14.1 Batch tests

Adsorption isotherm tests of phenols were performed using the traditional batch bottle technique [150]. The adsorption kinetics of phenol and \( p \)-nitrophenol onto carbon and wood samples were evaluated through controlled batch experiments. Sufficient volume of stock solution of known concentration was then placed on a temperature controlled bath to attain the desired temperature and to reach adsorptive equilibrium. Before the adsorbent is added to the reaction vials, a measured quantity of phenol was removed and a portion of that sample was analysed to determine the initial concentration in the aqueous solution. The concentration of adsorbent in each batch experiment is kept at 1.0g/l unless the adsorbent weight is specified (in dose studies it varied from 0.5 to 25 g). Temperature of the bath except isotherm and temperature studies was 293 K.

**Analysis:** Vials without sorbent were used as a control to ensure the negligible adsorption of phenol and \( p \)-nitrophenol on the surface of the glass vessels. At a given time interval a definite quantity of the overlying solution is withdrawn from each vial. The concentrations of phenol and \( p \)-nitrophenol were determined using UV/visible spectrophotometer at wave lengths 268 and 317 nm, respectively. For each kinetic experiment, the last sample was withdrawn after 360 minutes unless specified otherwise. For adsorption equilibrium experiments the contact time was set at 7 days. This time was considered to be adequate for phenol adsorption to reach equilibrium for microporous carbonaceous solids [2]. The effect of temperatures on adsorption of phenols was investigated using five different temperatures ranging between 283 and 323 K. The experimental procedure was exactly identical to that followed during kinetic study.

2.2.15 Adsorption of Metal ions

**Adsorbents:** Activated carbon CZ1 and oxidised carbon CZ1-26 were used to study the sorption of metals. These samples are characterized by very high surface acidity, acid strength, porosity and pore size distribution. The complete characterization (chapter 3 and 4) reveals that carbons behave like \( L \) type carbon with a greater proportion of carboxyl, phenolic, hydroxyl, carbonyl, lactonic and cyclic peroxide type groups. Modified wood FWD and GWD were also used to study the removal capacity towards metal ions.

**Adsorbates:** The toxicity of heavy metals, \( \text{Hg}^{2+} \), \( \text{Pd}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Cr}^{3+} \) and \( \text{Cr}^{6+} \) is well established. They are present in industrial wastewater discharges. Hence they have been selected to study adsorption phenomena on new sorbent surfaces. Potential toxicity, speciation and chemistry of the metal ions play an important role in their adsorbability.
2.2.15.1 Batch Tests

Batch techniques were carried out to study the adsorption of metal ions from aqueous solutions on carbon CZ1, oxidised carbon CZ1-26 and wood; FWD and GWD. A series of preliminary studies were conducted with varying amounts of sorbent and the volume of metal ion solutions to find the optimum volume to mass (V/M) ratio for the maximum uptake. Accordingly, a ratio of 1:200 for carbon and 1:100 for wood was found to be optimum. The full fledged adsorption experiments were conducted by keeping this relationship.

A number of glass bottles (Erlenmeyer flasks of capacity 100 ml) containing equal volumes of known concentrations of desired metal ions at constant pH, ionic strength and temperature were maintained. Accordingly, 20 ml solution of metal ion was shaken with 0.1 g of carbon or 0.2 g of wood. After a pre-determined time for adsorption, the solution was filtered.

Analysis: The concentration (mg/l) of metal ions in filtrate was measured using spectrophotometer. The equilibrium and kinetic experiments were conducted at 303 K. The residual concentrations of Hg$^{2+}$ ions was analysed by 1,10-orthophenanthroline-eosin method [151] whereas Pb$^{2+}$ and Cd$^{2+}$ ions were analysed by dithiozone [152] and pyronine G method respectively.

The analysis of Cr$^{6+}$ in solution was carried out spectrophotometrically by developing a purple violet colour [153] with 1,5-diphenyl carbazide in acidic solution. The total chromium was determined by oxidising any trivalent chromium with potassium permanganate, followed by analysis as hexavalent chromium. The difference between the total and hexavalent chromium concentrations are usually taken to represent the Cr$^{3+}$ concentration. In the present study, adsorption of Cr$^{3+}$ is done separately using standard working solutions similar to other metals. The estimation of Cr$^{3+}$ is done by oxidising the Cr$^{3+}$ present in the solution with acid-potassium permanganate followed by analysis as Cr$^{6+}$.

The concentration of metal ions was corrected for the loss of ions through adsorption on the walls of the glass bottles by running blank experiments. The equilibrium amount $q_e$ and fraction of ions adsorbed at any time $F(t)$ were determined according to the relations

$$q_e = C_i - C_f$$

$$F(t) = (C_i - C_f)/C_i$$

where $C_i$ is initial metal ion concentration (mg/l) in solution. $C_f$ metal ion concentration (mg/l) at time $t$. The distribution coefficient $K_D$ (ml/g) was calculated as,

$$K_D = \frac{C_i - C_f}{C_f} \times \frac{V}{M}$$
To find the equilibrium time and effect of agitation time on the adsorption of metal ions, 20 ml of solution containing 250 mg/l metal ion was shaken with 0.1 g (carbon) or 0.2 g (wood). The quantity of metal remaining in the supernatant solution was determined at various time intervals. The amount adsorbed was calculated and reported as $q_t$, $F(t)$, $K_D(t)$ or percentage. In all experiments, pH of each solution was measured before and after adsorption. An ionic strength of 0.01 M NaNO$_3$ was maintained for metals Pb$^{2+}$, Hg$^{2+}$ and Cd$^{2+}$. No electrolyte is used for Cr$^{6+}$ and Cr$^{3+}$. The effect of pH on metal ion adsorption on carbon and wood was studied using 250 mg/l. The pH of the solution containing Pb$^{2+}$, Hg$^{2+}$ and Cd$^{2+}$ ions was adjusted between 2.0 and 12.0 using 0.01 M HNO$_3$ and 0.01 M NaOH solutions. The adsorption system for pH study was kept till the equilibration time was achieved. The residual concentration and pH of the filtrate was noted to obtain the optimum pH for each adsorption system.

2.2.16 Summary of Experiments

The proposed experiments were designed to determine the rate mechanism and the effects of various parameters such as initial concentrations, pH, contact time, adsorbent dose, temperature and energetics on the adsorption. Only one grain size carbon and wood alone was used throughout the study. The mechanical method (sieve analysis) was used for the fractionation of the particle sizes used in the present study. The summary of experimental work in batch technique is presented in Table 2.1.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Description of experiment</th>
<th>Adsorbate; phenols/metals (mg/l)</th>
<th>Mean particle size</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon µm</td>
<td>Wood µm</td>
</tr>
<tr>
<td>1.</td>
<td>Effect of adsorbent dose</td>
<td>500</td>
<td>284.5</td>
<td>150.33</td>
</tr>
<tr>
<td>2.</td>
<td>Rate of adsorption</td>
<td>50, 100, 150, 250</td>
<td>284.5</td>
<td>150.33</td>
</tr>
<tr>
<td>3.</td>
<td>First order reversible kinetic fit</td>
<td>50, 100, 150, 250</td>
<td>284.5</td>
<td>150.33</td>
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<tr>
<td>4.</td>
<td>Mass transport studies</td>
<td>50, 100, 150, 250</td>
<td>284.5</td>
<td>150.33</td>
</tr>
<tr>
<td>5.</td>
<td>Effect of initial concentrations</td>
<td>50, 100, 150, 250</td>
<td>284.5</td>
<td>150.33</td>
</tr>
<tr>
<td>6.</td>
<td>Isotherms</td>
<td>50, 100, 250, 350</td>
<td>284.5</td>
<td>150.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500, 650, 750, 1000</td>
<td>284.5</td>
<td>150.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1500, 2000, 2500, 3000</td>
<td>284.5</td>
<td>150.33</td>
</tr>
</tbody>
</table>

The effect of temperature on adsorption was studied at 283, 293, 303, 313 and 323 K using an initial concentrations of 250 mg/l. The rate constants for the distinct stages of metal adsorption were determined.
The equilibrium isotherm studies were also performed over different aqueous metal concentrations. Data were analysed using standard isotherm equations. Hence, thermodynamic quantities such as $\Delta G$, $\Delta H$ and $\Delta S$ of adsorption process were evaluated.